

Nikel based perovskite catalysts supported on olivine particles for the steam gasification of biomass in a fluidized bed gasifier

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Introduction

Biomass feedstocks are the most abundant renewable materials on earth, and are considered by far the highest quality form of indirect solar energy. The use of biomass as a source of energy offers an opportunity for regional development, because they will contribute to the solution of the problem of electric power delivery to large areas of less developed regions, where biomass sources are abundant and electrification is poor. In recent years the attention is focused to the development of small electrical power plants that can be fed with the biomass produced near the location of the plant (1). Nowadays the most promising technology able to transform biomass in an energy vector that can be easily handled and efficiently transformed in electricity, is the gasification process that also allows to separate the pollutant before their total oxidation. To increase the efficiency of the biomass gasification processes, and decrease the heavy organic products, catalysts have been used in order to transform the hydrocarbons in light gases such as CO and H₂. Most of the catalysts used are commercial products developed for methane and naphtha reforming unable to be utilised directly into the fluidised bed because they are soft and their low density does not permit high biomass throughput to the gasifier. For this reason the catalysts are usually placed in a secondary fixed bed reactor after the gasifier. In this work we report the preparation, characterization and reactivity tests performed with a catalyst able to be utilised directly into the gasifier with the aim to simplify the overall biomass gasification process.

La-Ni-Fe perovskite catalyst supported on olivine particles

Most of the commercially available Ni catalysts display a moderate to rapid deactivation due to the build up of surface carbon and 'sintering' effects, that favour coke production. As far as the sintering problem is concerned, the active catalyst species have been inserted in a definite chemical structure, rather than just dispersing these on an inert support. Structure such as perovskite (ABO₃), in which A and B are compatible elements, have been employed. In this way, although the specific surface of the catalyst so obtained is less than in supported catalytic systems, the strong interactions between the various elements included in the structure limit the sintering of the active species as well as carbon build-up. In order to be able to carry out biomass gasification tests with the catalyst introduced into the fluidised bed, tri-metallic perovskites having the general formula LaNi_xFe_(1-x)O₃, with 0 < x < 1, were prepared by means of a sol-gel method. Nitrate salts (La(NO₃)₃·6H₂O, Ni(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O) were dissolved separately in hot propionic acid, stirred under reflux, and adapted to obtain the desired value of x. Nickel and iron propionic solutions were mixed and added rapidly to the lanthanum solution. The resulting solution was mixed for 30 minutes, olivine particles in the size range between 250 μm and 600 μm were added to these solutions and impregnated. The excess solvent (propionic acid) was slowly evaporated under vacuum (0.1 atm) at 60 °C. The support so impregnated was dried at 120 °C and then calcined under air (for 4 hours at 800 °C). The perovskite accounts for 4.5% of the total particle weight, as given by the elemental analysis. Figure 1 shows a comparison of the TPR curves of LaNi_{0.3}Fe_{0.7}O₃ impregnated on uncalcined olivine with that of olivine itself. Three reduction peaks are distinguishable for the La-Ni-Fe/olivine system, at 340°C, 550°C and 880°C. That at the intermediate temperature level (550°C) clearly corresponds to the reduction peak exhibited by olivine (630°C), and the temperature gap between the two has to be related to the effect of Ni on the olivine structure. The small peak at 340°C can be either related to the reduction of nickel oxide to form free Ni particles, or to an oxygen loss by the structure. The peak at 880°C is similar to that encountered in the reduction of the LaNi_{0.3}Fe_{0.7}O₃ solid solution and leads to metallic nickel; some metallic iron can be generated as well by the olivine structure forming a Ni-Fe alloy.

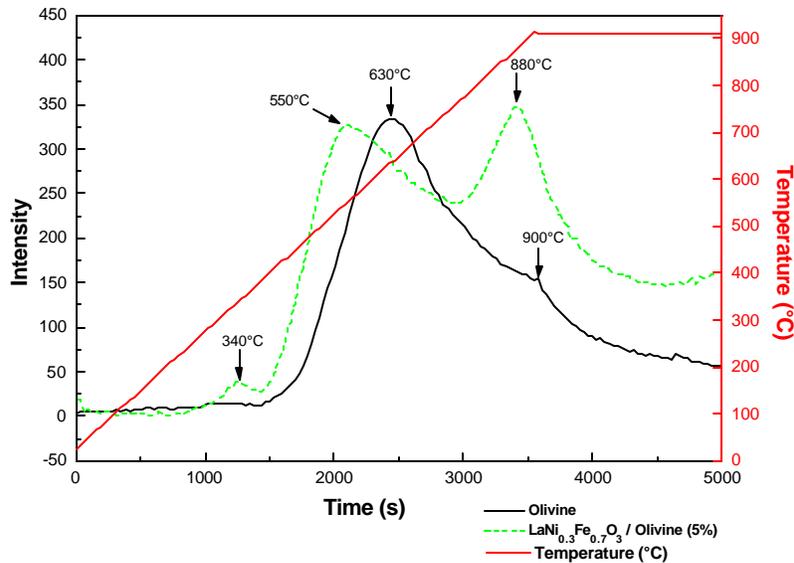


Figure 1. TPR curves for $\text{LaNi}_{0.3}\text{Fe}_{0.7}\text{O}_3/\text{olivine}$ and olivine.

Experimental results and conclusions

The experimental, bench-scale equipment utilized to perform the biomass gasification tests has been described elsewhere (2). For all runs, the gasifier bed was charged with 600 g, either of olivine particles, or else of perovskite catalyst supported on olivine as described in a previous section. For each gasification run the biomass feed rate was fixed at 0.3 kg h^{-1} and the steam/biomass feed ratio at unity. The effective gas contact time, defined as the particle-free volume in the fluidized bed divided by the overall gas volumetric flow rate under reaction conditions, can be estimated to be close to 0.25 sec. In Table 1 we report the operating conditions and some results obtained using $\text{LaNi}_{0.3}\text{Fe}_{0.7}\text{O}_3$ deposited on calcined olivine.

Table 1. Operating conditions and results of the catalytic tests

run number	bed inventory	gasification temperature,	tar content $\text{g m}^{-3}\text{n}$ of dry gas	dry gas yield in m^3n per kg of daf biomass	pre-reduction treatment
A0	olivine	820	0.55	1.86	----
A1	catalyst	790	0.89	1.79	no
A2	catalyst	820	0.32	1.95	yes
A3	catalyst	830	0.25	1.95	yes

Overall, the results show that when the plant is operated with fresh, pre-reduced catalyst a gaseous product with low tar content is obtained: this is particularly noteworthy in view of the remarkable simplicity of the process configuration. The carbon deposited on the catalyst after all the runs is $< 30 \text{ ppm}$. The elemental analysis determinations after tests resulted in a concentration of perovskite on olivine of 3.6 wt%, (instead of 4.5 wt% as measured in the fresh catalyst) suggesting a progressive loss of the active perovskite layer deposited on the olivine particles due to abrasion and attrition. Further efforts are therefore required to improve the catalyst impregnation process in order to make it able to withstand the high temperature fluidization environment and so be suitable for industrial applications.

References

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- [2] Rapagnà S, Jand N, Kiennemann A, Foscolo PU, Biomass & Bioenergy [19 \(3\)](#) 2000, p. 187.